Missing xy-Band Fermi Surface in 4d Transition-Metal Oxide Sr_2RhO_4: Effect of the Octahedra Rotation on the Electronic Structure

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Electronic structures of the 4d transition-metal oxide compound Sr_2RhO_4 are investigated by angle-resolved photoemission spectroscopy and density-functional electronic structure calculations. In the measured Fermi surfaces (FS) of Sr_2RhO_4, the xy-band FS sheet expected from the well-established results of the FS of Sr_2RuO_4 is missing, the volume of which should be different only by one additional electron for Sr_2RhO_4. The apparent contradiction is resolved by a careful analysis of the band structure where the rotation of octahedra results in the hybridization of e_g and t_{2g} states and thus plays a key role in the determination of the electronic structure near E_F. The modification of the FS structure due to the distorted lattice is related to the charge transfer among the orbital states and suggested to be relevant to the metal-insulator transition in $Ca_{2-x}Sr_xRuO_4$.

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The interplay among on-site Coulomb interactions, electronic band structure, and lattice distortions in 3d transition-metal oxides (TMO) has been widely discussed in the context of electron correlations and metal-insulator transition (MIT) [1], while the issues in 4d TMO are rather subtle due to the extended character of the 4d states. Recently, MIT observed in $Ca_{2-x}Sr_xRuO_4$ (CSRO) [2] has brought much attention to the importance of strong electron correlations in the 4d TMO series. By substituting isovalent Ca ions, the superconducting parent compound Sr_2RuO_4 [3] evolves into a correlated metal ($0.2 \leq x \leq 0.5$), and eventually transits to a Mott insulator ($x \leq 0.2$). The migration of the ground state from a weakly correlated metal to a Mott-insulator is accompanied by the structural distortions including the in-layer rotation and tilting of RuO_6 octadedra induced by the cation substitutions [4].

A well-known classical example of how the structural distortions lead to different electronic ground states is V_2O_3 and its derivatives [5], where it is believed that the overall band structures remain intact and only the bandwidth W is significantly affected by the structural distortions, and controls the MIT. Theoretical calculations along this line incorporating dynamical mean-field theory (DMFT) are believed to capture the essential features of the MIT in 3d TMOs [6].

However, there exist subtle differences in the 4d TMOs. 4d orbitals have larger spatial extent and become strongly hybridized with neighboring ligand orbitals. As a result, the bandwidths are considerably larger than in 3d TMOs and the electronic structures are more susceptible to the structural distortions. The effects of the structural distortions on the electronic band structures may be more than just bandwidth narrowing, especially in the presence of multiple orbital degrees of freedom.

The recent theoretical study on 4d CSRO by Anisimov *et al.* predicted an interesting possibility of orbital-selective Mott transition (OSMT) [7]. Based on the DMFT calculations, they argued that the transition occurs in an orbital-dependent way, leading to the coexistence of localized and itinerant bands. However, such results were obtained by modeling the system as bandwidth-controlled MIT; the orbital-selective gap opens as U is increased. The subsequent experimental evidences against the OSMT scenario [8,9] raise a question that the model lacks some key ingredients.

Ca doping up to $x = 0.5$, at which the alleged OSMT occurs, induces mostly the in-layer rotation of the octahedra which brings most of the changes in the electronic structure and is in large part responsible for the MIT in CSRO. The most direct way to study the evolution of the electronic band structures is by angle-resolved photoemission study (ARPES). However, Ca doping causes discomforting effects in ARPES measurements possibly by creating disorders; the signals from the Ca doped systems are in general very weak and broad.

The recent synthesis of Sr_2RhO_4 (SRhO) single crystal [10], which is isostructural to CSRO, presents an opportunity to study the effects of rotation without disorders, since the octahedra is already rotated by ≈10° in the parent compound. Although SRhO has one more d electron than CSRO, SRhO bears many similarities with CSRO [11] and hence one may gain much insight from comparative studies of the two. In this Letter, we present the ARPES and band calculation studies of the electronic structure of SRhO. The measured band structures of SRhO are found to be surprisingly different from those of Sr_2RuO_4. Through the analysis of the band structure and the effect of the symmetry change, it is found that a dramatic change of the FS can occur. This implies that the octahedra rotation in 4d TMOs has a profound effect on the electronic structures, which is to be discussed in connection with the MIT in CSRO.

ARPES data were taken at BL7 in the Advanced Light Source and at BL5-4 in the Stanford Synchrotron Radiation Laboratory. The photon energy used for the FS mapping was 85 and 22 eV and the total energy and angular resolutions at 22 eV were about 15 meV and 0.4°, respectively. Sr_2RhO_4 single crystals were cleaved *in situ* at a pressure better than 5×10^{-11} torr and at 20 K. The electronic band structures of Sr_2RhO_4 were calculated by using the full-potential linearized augmented plane wave (FLAPW) method within the local-density approximation [12]. For the calculations of the distorted Sr_2RhO_4, we used the $I4_1/acd$ structure with $a = 5.436$ Å and $c = 25.775$ Å [13], whereas tetragonal $I4/mmm$ symmetry was assumed for the undistorted phase. The k-point summations during the self-consistency iterations were done by the tetrahedron method with 99 k points within the irreducible Brillouin zone.

Since our discussions will depend on the comparisons of the electronic structures of SRhO with the Sr end member of CSRO, Sr_2RuO_4 (SRuO), it will be helpful to briefly compare the structural or electronic configurations of the two compounds at the outset. Structurally, both SRuO and SRhO crystallize in the layered perovskite K_2NiF_4 structure with elongated octahedra along c axis, the only difference being that the octahedra in SRhO are rotated by $\approx 10°$ about the c axis, which lowers the symmetry and transforms the original 2D Brillouin zone of 1×1 square lattice into the $\sqrt{2} \times \sqrt{2}$ lattice rotated by 45° [13]. SRhO has one more d electron than SRuO, so that it contains five d electrons in the t_{2g} manifold assuming a low-spin configuration, as usual in 4d oxides. In the first approximation, SRhO can be regarded as SRuO with one additional electron. The FSs of SRhO may then be predicted by a rigid shift of the Fermi level in the band structure of SRuO [14], which should give FSs qualitatively similar to those of SRuO. In addition, SRhO is expected to have "shadow" FSs due to the zone folding.

Figure 1 shows (a) the selected energy distribution curves (EDC) along high symmetry lines and (b) the FS constructed from them by taking the ARPES spectral intensity at E_F. Two dispersing bands α and β are identified by the topology of the FS they compose and comparison with that of the SRuO. In SRuO, it is known that four electrons are equally populated among the three t_{2g} orbitals which form three sheets of FSs; one-dimensional (1D) α and β sheet derived from yz/xz band and 2D γ sheet from the xy band [15]. The occupation of one more electron would increase the volume of electronlike β and γ sheets and shrink holelike α sheet. However, as shown in Fig. 1, the FSs of SRhO are not like what are expected from the naïve rigid band model. The main difference is that the γ sheet is *absent* in SRhO, implying the full occupation of the xy band. The FS volumes of the α and β sheets are 0.02 and 0.52, respectively, which add up to theoretical value of 1 hole per unit cell. Thus the absence of γ sheet is not due to failure of detection that could arise due to matrix element effects.

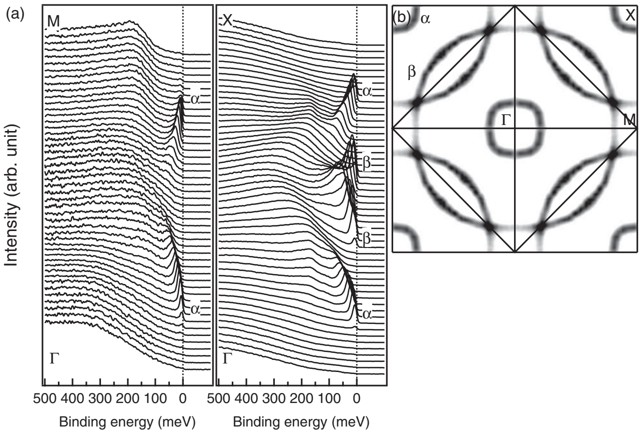

FIG. 1. (a) EDCs along the high symmetry lines and (b) Fermi surface of Sr_2RhO_4 obtained by integrating the ARPES spectra in the energy window of 10 meV centered at E_F. For simplicity, we use the Brillouin zone and notations of the undistorted structure. True Brillouin zone is shown by the smaller rotated square box in panel (b).

Considering the crudeness of the model, the failure to correctly predict the FSs of SRhO may not be surprising. However, it is still unexpected that the xy orbital band is fully occupied, in view of the fact that the 2D xy orbital band has wider bandwidth than other 1D t_{2g} bands and the xy orbital state is located above yz/zx states by the crystal field. Whether the band-structure calculation performed on SRhO would correctly predict the measured FSs is one question, but more importantly how the electron configuration of fully occupied xy band is realized is of fundamental interest, as it is of direct relevance to the problem of MIT in multiband CSRO as discussed earlier. The only difference in the structures between SRuO and SRhO is the rotation of the octahedra, and hence one may regard that the unexpected electronic configuration in SRhO results from the rotational distortion.

To address this issue, we have performed band-structure calculations with artificial undistorted crystal structure, i.e., with rotation angle set to zero while keeping the lattice constants constant. Figure 2(a) shows the FSs obtained by the calculation done with undistorted crystal structure. The FSs indeed have topologies that are consistent with that of the SRuO; expanded β and γ sheets and shrunk α sheet. One difference in the calculated FSs is that there exists a small electron pocket around Γ (assigned as δ sheet) which is derived from filling an e_g band as will become evident later. Now, let us consider the effect of rotation. Because of the $\sqrt{2} \times \sqrt{2}$ lattice, the X point becomes equivalent to the Γ point and the band structure repeats itself in the reciprocal space according to the new lattice symmetry. If the rotation does not change the band structures appreciably,

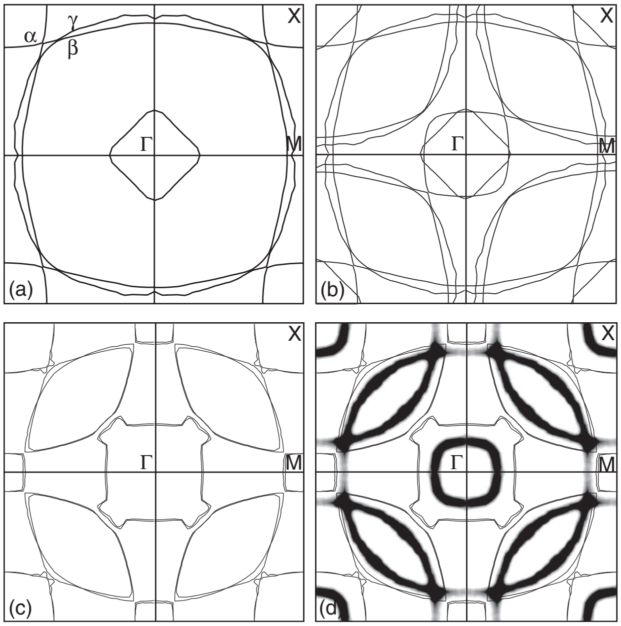

FIG. 2. (a) Calculated FSs in the undistorted structure. (b) Expected FSs due to zone folding in the reduced symmetry (band structures are assumed to be unaffected by the rotation). (c) FSs in the real structure. (d) Overlay of the calculated and measured FSs.

the new FSs under the rotation then can be constructed by shifting and overlaying the FSs in Fig. 2(a) on the original FSs so that the shifted X coincides with the original Γ, as shown in Fig. 2(b). It is exactly analogous to the case of band foldings in SRuO by of the symmetry lowering due to the surface reconstruction [15].

However, the calculated FSs of the real crystal structure, shown in Fig. 2(c), are qualitatively different from that in Fig. 2(b); now the γ is missing as in the measured FSs. Figure 2(d) shows the overlay of calculated and measured FSs, which are in overall in good agreement. However, there are some minor differences in the shapes and volumes of the FS sheets. These differences may be attributed to electronic correlation effects and disorders in the rotation directions between the layers which are not taken into account in the calculation. We leave the issue on the role of correlation and disorder effects to future studies, and here we discuss in detail the mechanism by which the γ band disappears by the rotational distortion.

Finding out the distortion effects on the electronic structure requires a careful analysis of the band structure. Figure 3(a) shows the band structure along the high symmetry lines near E_F in the undistorted structure. The most notable feature is the dispersion of the $x^2 - y^2$ band down to below E_F, which gives rise to a small electron pocket around Γ. As we shall see, this feature has profound implications on the electronic structure through the hybridization with t_{2g} states. In Fig. 3(b), we plot the folded bands that would appear in the lowered symmetry (dashed line) in addition to the original bands in the undistorted structure (solid line) [16]. We plot the band structure in real structure in Fig. 3(c) [17]. Comparison of Fig. 3(b) and 3(c) shows that most part of the band structure in panel (c) can be understood in terms of the bands in the undistorted structure and their replicas. Especially, the yz/zx and $3z^2 - r^2$ bands are not affected much by the rotational distortion apart from the constant shift in the energy. On the other hand, the xy and $x^2 - y^2$ bands undergo significant changes. For clear presentation, we plot in Fig. 3(d) and 3(e) only the xy and $x^2 - y^2$ bands in colors. The folding of the bands results in an overlap of the xy and $x^2 - y^2$ bands which are no longer orthogonal in the rotated geometry. The hybridization between the two leads to the formation of a gap between the bonding and antibonding bands, which no longer cross the Fermi energy. Therefore, the rotational distortion (i) mixes the otherwise orthogonal xy and $x^2 - y^2$ bands, (ii) opens a gap between the two, and (iii) consequently pushes the xy band below the Fermi energy.

The vanishing of the γ and δ sheets upon the octahedra rotations can be understood as filling of the unoccupied part of the xy band by the occupied part of the $x^2 - y^2$ band. However, the area of δ sheet is not large enough to fill the unoccupied part of the γ sheet, and thus the complete filling of the xy band is accomplished through the transfer of the electrons from the yz/zx band. This point is clearly illustrated in Fig. 4(a), which shows the projected

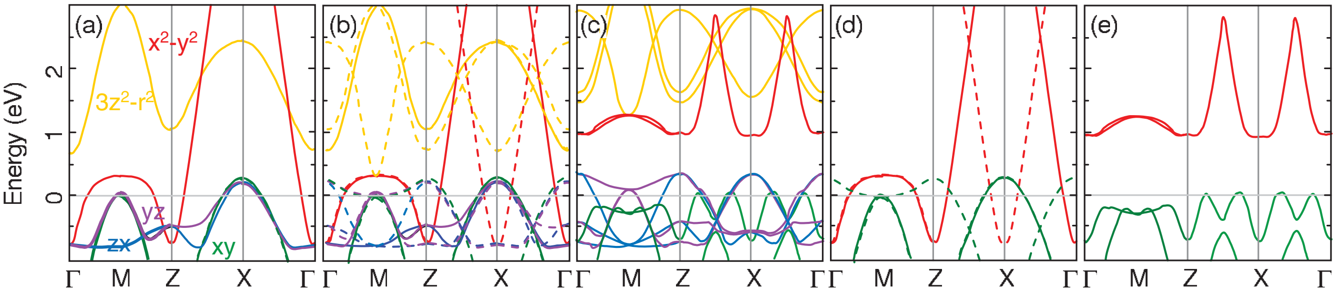

FIG. 3 (color). Band structure (a) of the undistorted and (b) distorted structures. Solid and dashed lines are the original and folded bands, respectively. (c) Band structure in the real structure. In panels (d) and (e), only the relevant bands in panels (b) and (c) are highlighted.

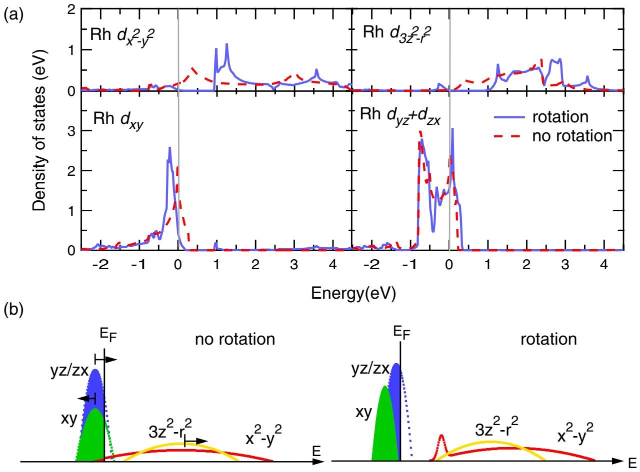

FIG. 4 (color online). (a) Projected partial density of states in the crystal structure with and without the rotation. The solid (dashed) line represents the PDOS in the distorted (undistorted) structure. (b) Schematic diagram of the band shifts due to the distortion.

partial density of states (PDOS) of d states in the structures with and without the rotation. By the rotation, the PDOS of $x^2 - y^2$ state becomes gapped to form bonding-antibonding bands through the hybridization with the xy band. The center of the antibonding band shifts upward from 1.7 eV to 2.0 eV. Concurrently, the xy PDOS is narrowed and its major peak is shifted downward from 0 eV to -0.25 eV, while yz/zx band suffers weight transfer from below to above E_F, implying transfer of electrons from yz/zx band to xy band. Again, this PDOS analysis confirms the importance of the e_g states in the determination of the electronic structures near E_F. It is also noted that the PDOS of the $z^2 - r^2/3$ component just above E_F, which is shifted up by 1 eV by the rotation, is attributed to the symmetry mixing of $z^2 - r^2/3$ with $x^2 - y^2$ around the M point of the Brillouin zone. The schematic diagram in Fig. 4(b) summarizes the above key features derived by the distortion.

Our findings should have strong implications in the model for the CSRO system. In the effective models for the description of 4d Ru or Rh compounds, it is widely accepted that consideration of only the t_{2g} manifold is necessary as the e_g states are considered to be irrelevant due to the large crystal field separation. However, what we have demonstrated through the analysis of the FS of SRhO indicates that the presence of the wide band e_g states near the Fermi level can contribute to the change of the electronic structure upon the symmetry change, e.g., the rotation of octahedra, which allows the hybridization of $x^2 - y^2$ and xy bands. In fact, the hybridization of $x^2 - y^2$ and xy bands near the Fermi level can be more effective than the crystal field splitting among the three t_{2g} orbitals. It should be noted the $x^2 - y^2$ band disperses almost down to the E_F also in the band structures of SRuO. Consequently, the symmetry change due to the rotation of octahedra should lead to electron transfer from the yz/zx band to the xy band by the rotation induced by Ca-doping in CSRO system. The ARPES study of CSRO system for $x = 0.5$ sample [8] shows that the γ sheet turns from electronlike to holelike, which implies increase in the occupation of the xy band. The same behavior is also observed in the surface states of the SRuO in which the octahedra are rotated [15,18].

It is noted that the increase in the xy band occupation is contradictory to the OSMT scenario which requires a half-filled xy band. It is suggested from our studies of SRhO that any theoretical model that describes MIT in CSRO should take into the effects brought about by the hybridization between t_{2g} and e_g states. CSRO may not be a simple bandwidth-controlled system; (1) the bandwidth of the xy band does not simply depend on the bond angle between metal and ligand ion, and (2) the systematic transfer of electrons from one band to the other may be an important factor in understanding the problem of MIT in a multiband system.

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[1] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
[2] S. Nakatsuji and Y. Maeno, Phys. Rev. Lett. **84**, 2666 (2000).
[3] Y. Maeno *et al.*, Nature (London) **372**, 532 (1994).
[4] M. Braden, G. André, S. Nakatsuji, and Y. Maeno, Phys. Rev. B **58**, 847 (1998).
[5] J.H. Park *et al.*, Phys. Rev. B **61**, 11 506 (2000).
[6] A. Georges, G. Kotliar, W. Krauth, and M.J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
[7] V. Anisimov, I. Nekrasov, D. Kondakovl, T. Rice, and M. Sigrist, Eur. Phys. J. B **25**, 191 (2002).
[8] S.-C. Wang *et al.*, Phys. Rev. Lett. **93**, 177007 (2004).
[9] H.J. Noh *et al.*, Phys. Rev. B **72**, 052411 (2005).
[10] I. Nagai *et al.* (to be published).
[11] For example, they show very similar behavior in the transport measurements. See Ref. [10].
[12] H.J.F. Jansen and A.J. Freeman, Phys. Rev. B **30**, 561 (1984).
[13] T. Vogt and D.J. Buttery, J. Solid State Chem. **123**, 186 (1996).
[14] I. Hase and Y. Nishihara, J. Phys. Soc. Jpn. **65**, 3957 (1996).
[15] A. Damascelli *et al.*, Phys. Rev. Lett. **85**, 5194 (2000).
[16] For simplicity, we keep the notation of the undistorted structure.
[17] Our calculation reproduces the earlier band calculation results by Hase *et al.*. See Ref. [14].
[18] R. Matzdorf *et al.*, Science **289**, 746 (2000).